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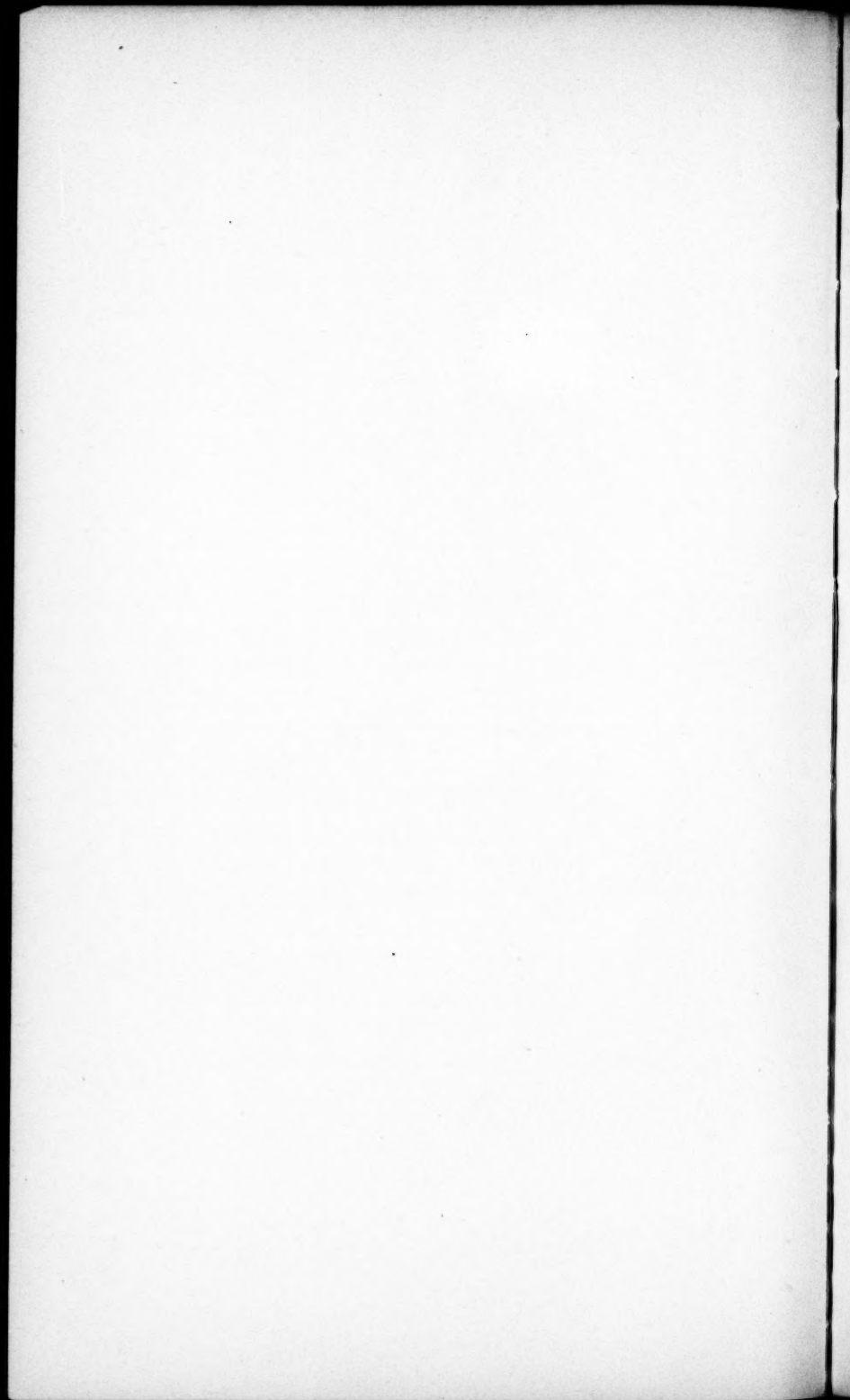
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF HARVARD COLLEGE.

*THE QUANTITATIVE DETERMINATION OF ARSENIC  
BY THE GUTZEIT METHOD.*

BY CHARLES ROBERT SANGER AND OTIS FISHER BLACK.

WITH TWO PLATES.



## THE QUANTITATIVE DETERMINATION OF ARSENIC BY THE GUTZEIT METHOD.

BY CHARLES ROBERT SANGER AND OTIS FISHER BLACK.

SEVERAL attempts have been made to apply the so-called Gutzeit reactions to the quantitative determination of arsenic, especially in England since the epidemic in 1900 of arsenical poisoning from beer.

Kelynack and Kirkby<sup>1</sup> suggested that an approximate valuation of the amount of arsenic in a sample of beer may be made by comparing the stain produced on mercuric chloride paper by the arsenical hydrogen from a given portion of the sample with that produced by a definite quantity of a standard solution of arsenic.

Bird<sup>2</sup> made a careful study of the conditions under which the arsenical stain on mercuric chloride paper may be best obtained and identified, with especial reference to the interference of the hydrides of sulphur, phosphorus, and antimony. Although his work is extremely suggestive of a quantitative application, he himself considers that the test is only approximately quantitative, in that the stain obtained from a given amount of substance, say beer, may be shown to be greater or less than the stain representing a fixed limit of arsenic for that amount. He also regards it as a true negative test.

Treadwell and Comment<sup>3</sup> compared the stain obtained from the action of arsine on argentic nitrate paper with a series of stains from definite quantities of a standard solution of arsenic. The method, applied by these authors to the detection of arsenic in mineral waters, is said to have given good results.

Dowdard,<sup>4</sup> after describing a modification of the Gutzeit test which allows the detection of minute traces of arsenic in a small volume of solution, suggested the preparation of a standard set of stains, which should be kept in a tightly stoppered bottle in a dark place.

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<sup>1</sup> Arsenical Poisoning in Beer Drinkers, p. 88. London, Ballière, Tindall, and Cox, 1901.

<sup>2</sup> Analyst, **26**, 181 (1901).

<sup>3</sup> Treadwell, Kurzes Lehrbuch der Analytischen Chemie, **2**, s. 138 (1902).

<sup>4</sup> Chem. News, **86**, 3 (1902).

Thomson<sup>5</sup> attempted to make the reaction quantitative by passing the arsenical hydrogen through a tube in which was hung a cotton thread or a paper, saturated with mercuric chloride solution, which, from the intensity of the stain produced upon it, should show the amount of arsenic present. Thomson states, however, that his results were untrustworthy.

Goode and Perkin<sup>6</sup> made a series of experiments to ascertain if the Gutzeit test could be made quantitative, and if a set of standards could be prepared which should be at least as permanent as the standard mirrors of the Berzelius-Marsh process. Stains were made as usual on paper treated with mercuric chloride, but the impossibility of making them permanent led to their abandonment for quantitative purposes, except that a given stain might be matched with freshly prepared standards.

Langmuir,<sup>7</sup> in order to detect the presence of undecomposed arsine in the Marsh test, placed in the end of the exit tube a slip of paper moistened with a saturated solution of mercuric chloride. It apparently did not occur to him that this might also be used quantitatively, but he seems to have employed the ordinary color stains successfully in the approximate analysis of glycerine for arsenic.

Aside from the above-quoted authors, there are doubtless many who have been able to use the Gutzeit reactions as a means of approximate analysis, but we have not met with a careful study of the conditions under which the reactions may be employed quantitatively with any degree of accuracy.

The chief difficulty in differentiating between stains caused by various amounts of arsine on either argentic nitrate or mercuric chloride paper lies in the fact that the action is partly over the surface and partly within the fibre of the paper. Further, a single layer of paper is not always sufficient to retain all the arsenic evolved, and stains from equal amounts of arsine may not always be of the same density. These difficulties disappear almost entirely if one allows the arsenical hydrogen to act not against, but along a surface. The principle, therefore, of the modification we suggest in order to make the Gutzeit reactions more accurately quantitative, is to allow the arsine to pass over a strip of paper impregnated with mercuric chloride and to compare the band of color thus obtained with a series of bands prepared from known amounts of a standard solution of arsenic. We think that

<sup>5</sup> Royal Commission on Arsenical Poisoning, Final Report, 2, 58. London, Eyre and Spottiswoode, 1903.

<sup>6</sup> Jour. Soc. Chem. Ind., 25, 507 (1906).

<sup>7</sup> Jour. Amer. Chem. Soc., 21, 133 (1899).



the failure of Thomson to get good results was merely due to unsuitable conditions.

Our experience has not only confirmed the conclusion which has been reached by most of those who have investigated the Gutzeit reactions, that the use of mercuric chloride is preferable to that of argentic nitrate from a qualitative standpoint, but it has also shown that the former reagent is the one better suited to the quantitative analysis.

A careful study of the conditions of the reaction, following the principle stated above and made for the most part without knowledge of the work of the above-quoted authors, has shown that the reaction can be made the basis of a simple and fairly accurate quantitative method with no more than ordinary analytical precautions.

#### THE METHOD.

*Sensitized Mercuric Chloride Paper.* For this purpose we used at first a smooth filter paper of close texture, but we have recently employed to greater advantage a cold pressed drawing paper made by Whatman. The latter not only gives better color results, but also, on account of its greater strength, withstands better any subsequent treatment for development or identification of the color. A square meter of this paper weighs about 160 grams (4 1-4 ounces per square yard). It is cut into strips having a uniform width of 4 mm., and we use for this purpose a carefully made brass rule of exactly this width. The cutting may be done with a sharp knife, but more accurately and in large quantity by the machine which should be accessible at any printing office.

The strips, which must be clean and free from dust, are sensitized by drawing them repeatedly through a five per cent solution of recrystallized mercuric chloride until they are thoroughly soaked. They are then placed to dry on a horizontal rack of glass rods or tubing, and, when dry, are at once cut into short lengths of 7 cm., discarding the ends by which the strips were held during the immersion. A bundle of these strips is placed in a stoppered tube or bottle containing calcic chloride covered by cotton wool, and is kept in the dark until needed.

*The Reduction Apparatus.* (See Figure A.) This consists of a glass bottle of 30 c.c. capacity, closed by a pure rubber stopper with two holes. Through one of these holes passes a small thistle tube, about 15 cm. long, reaching to the bottom of the bottle and constricted at its lower end to an opening of about 1 mm. The other hole carries an exit tube bent first at a right angle, then back again in the same

plane in the form of a C. To this is fastened by means of a rubber stopper a short bulb tube about 12 mm. in diameter, terminating in a longer tube which has a bore of slightly over 4 mm. The bulb of this tube (deposition tube) is loosely filled with clean absorbent cotton which has been kept over sulphuric acid to insure uniform dryness. Instead of the bulb tube, the rubber stopper of the exit tube may carry a short piece of glass tubing of about 12 mm. diameter, in which is placed the absorbent cotton, and to which, by means of another rubber stopper, is attached the deposition tube.

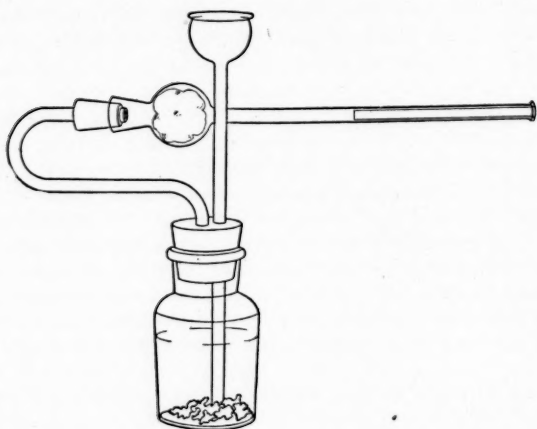


FIGURE A.

The simplicity and compactness of this apparatus allow a number of determinations to be carried on at the same time by the use of several pieces. It is important, however, that the bottles be of the same size, and it is also advisable to have the rest of the apparatus of as nearly definite size as possible.

*Reagents.* We have used zinc and hydrochloric acid in preference to zinc and sulphuric acid, as the action goes on more regularly and without the addition of a sensitizer. The chance for the formation of hydrogen sulphide is also less. The zinc, known as Bertha spelter, is from the New Jersey Zinc Company of New York, and has been proved by exhaustive tests to be free from arsenic. It contains not over 0.019

per cent of lead and not more than 0.013 per cent of iron. The hydrochloric acid is obtained of the Baker and Adamson Company of Easton, Pennsylvania, and has been shown by careful analysis to contain not over 0.02 milligram of arsenious oxide per liter. The dilution employed, one part of acid to six of water, is equivalent to a normality of about 1.5. The quantity of diluted acid used in the analysis would not contain over 0.00004 mg. of arsenious oxide, an amount beyond the practical limit of the delicacy of the method.<sup>8</sup> No evidence of sulphur, phosphorus, antimony, or arsenic has been obtained from these reagents when used in long continued blank tests.

*Procedure.* Three grams of carefully and uniformly granulated zinc are placed in the bottle, and a strip of sensitized paper is slipped into the deposition tube to a definite distance, the paper being wholly within the tube. Fifteen cubic centimeters of diluted acid are then added through the thistle tube, and the evolution of hydrogen is allowed to continue for at least ten minutes. At the end of this time the rate of flow of the gas has become as regular as possible, and the atmosphere in the deposition tube has a nearly definite degree of saturation with aqueous vapor. On these two conditions depends chiefly the uniformity of color bands from equal amounts of arsenic. In this time, also, the absence of arsenic in reagents and apparatus is assured, in the great majority of cases, by the non-appearance of color on the sensitized paper, but the blank test may be as long continued as circumstances demand.

The solution to be tested is then introduced, either wholly or in aliquot part, which may be determined by weighing or measuring. In the former case we use a side-neck test tube of about 30 c.c. capacity, and weigh to the second decimal place. Unless the amount of arsenic be exceedingly small, it is not necessary to add the whole of the solution, but in that case the volume must be obviously not over 15 c.c., on account of the capacity of the bottle.

After introduction of the solution the color appears upon the paper in a few minutes and the deposit reaches its maximum within thirty minutes. The band of color thus obtained is then compared with a set of standard bands. From the amount of arsenic as estimated from the comparison, and the amount of solution from which the band was obtained, the calculation of the arsenic in the entire solution is simple.

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<sup>8</sup> We are also indebted to the Baker and Adamson Company for a preparation of hydrochloric acid containing a still smaller quantity of arsenic, the use of which will be later explained in the discussion of the absolute delicacy of the method.

*Standard Color Bands.* A standard solution is made by dissolving one gram of re-sublimed arsenious oxide in a small quantity of sodic hydroxide free from arsenic, acidifying with sulphuric acid and making up to one liter with recently boiled water. Of this solution (I) 10 c.c. are diluted to a liter with freshly boiled water, giving a solution (II) which contains 0.01 mg. or 10 micromilligrams (mmg.) of arsenious oxide per cubic centimeter. In testing the delicacy of the method we have also prepared solutions containing 1 mmg. (III) and 0.1 mmg. (IV) per cubic centimeter.

From definite portions of solution II, measured from a burette, a series of color bands is made by the above procedure, using a fresh charge of zinc and acid for each portion. Figure 1 (Plate 1) shows in colors the actual size of the set of bands made by us, corresponding to the following amounts of arsenious oxide in micromilligrams: 2, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70. The color in the lowest values is a lemon yellow, shading from this to an orange yellow and through orange yellow to reddish brown in the higher values.

*Preservation and Development of the Color Bands.* The rapid fading of the stains has been a serious obstacle to the use of the Gutzeit reaction for a quantitative method, and it became very soon evident to us that some means of preserving the color bands must be found before the method could be considered an entirely practical one. It was clear that the chief factors in the change of color were light and moisture, the latter being by far the more important. Concerning the mechanism of the reactions, either for the formation of the color or for its decomposition with water, the work of those who have investigated the reactions was not sufficient to guide us.

The early work of Rose<sup>9</sup> on the action of arsine on excess of mercuric chloride in solution showed that a yellowish brown precipitate was formed having the empirical formula  $\text{AsHg}_3\text{Cl}_3$ . This was considered by Rose to be made up of mercurous chloride and a compound of mercury and arsenic, to which the formula  $\text{As}_2\text{Hg}_3$  might be given.

Mayençon and Bergeret<sup>10</sup> consider the compound to be a mixture of arsenic and mercurous chloride.

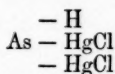
Franceschi,<sup>11</sup> apparently without knowledge of Rose's work, passed arsine through an aqueous solution of mercuric chloride. The liquid became at first a light yellow, then red, and there was precipitated a substance at first yellow, but with excess of gas a dark red, "of the

<sup>9</sup> Pogg. Annal., **51**, 423 (1840).

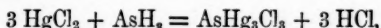
<sup>10</sup> Comptes Rendues, **79**, 118 (1874).

<sup>11</sup> L'Orosi, **13**, 289 (1890).

color of Spanish tobacco." For this compound Franceschi assumes from the analysis and properties the formula  $\text{AsHHg}_2\text{Cl}_2$ , which he writes:

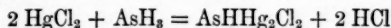


Lohmann,<sup>12</sup> who does not mention the results of Franceschi, finds the reaction to run in a similar manner. But the red product decomposed with water, becoming black, and with such rapidity that an analysis was impossible except through the decomposition products. From this the formula  $\text{AsHg}_3\text{Cl}_3$  was assigned. Lohmann considers that the reaction is always

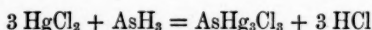


whether the precipitation is complete or not, and that the decomposition of the product depends (*a*) on the presence of mercuric chloride, in which case arsenic and mercurous chloride are the products, or (*b*) on absence of mercuric chloride, in which case mercury, arsenious acid, and hydrochloric acid are the products.

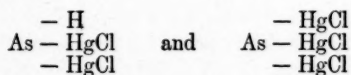
Partheil and Amort<sup>13</sup> note the formula given by Franceschi,  $\text{AsHHg}_2\text{Cl}_2$ , but evidently assume that it was for the yellow body (if such indeed exists) and not for the red, which was clearly indicated from Franceschi's paper. On this assumption and from Lohmann's work, they consider that the following is the reaction for the formation of the yellow body:



and for the red:



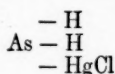
These reactions were given by Franceschi and by Lohmann respectively, but both of these authors were dealing with the red body. Partheil and Amort further consider these bodies to have the following structure, respectively:



<sup>12</sup> Pharm. Zeitung, **36**, 748 and 756 (1891).

<sup>13</sup> Ber. d. deutsch. Chem. Gesell., **31**, 594 (1898).

Passing excess of arsine through the solution in which the red body is suspended, Partheil and Amort obtain a black precipitate to which they give the formula  $\text{As}_2\text{Hg}_3$ , and this derives support from the reactions with alkyl iodides described by these authors in a succeeding paper.<sup>14</sup> The investigation is given somewhat more fully in a later paper by Partheil.<sup>15</sup> On partial precipitation of a mercuric chloride solution by arsine, a yellow body was obtained, to which, from a single analysis of an evidently impure substance, the formula  $\text{AsH}_2\text{HgCl}$  was assigned. From this experiment and from the results of Franceschi and of Lohmann, Partheil considers that there should be added to the two substances given above a third, with the structure



While the evidence appears to show that the hydrogen of arsine is replaced by the mercurous chloride group to a greater or less extent, the formula for the red substance does not seem to us to have been conclusively proved, and the reactions of decomposition are decidedly in doubt. Nothing has been brought forward to show definitely the relation of the yellow compound or compounds, if such exist, to the red. Lack of time prevents us at present from studying the reaction quantitatively, but it is hoped that the investigation may be taken up later by one of us. Nevertheless the following qualitative reactions have made it possible to treat the bands of color so that they may be kept for a considerable time, either in their original form or by means of a *quasi* development and fixation.

The removal of the relatively large excess of mercuric chloride from the paper by treatment with absolute ether or alcohol did not offer a solution of the difficulty, as the colors faded rapidly even when kept in the dark and over sulphuric acid. The color is quickly bleached by boiling with water, as is well known. Cold water acts more slowly, the color not being completely changed until after a day or two, and then not bleached, but converted to a dull gray. Bird,<sup>16</sup> and also Goode and Perkin,<sup>17</sup> have observed the action of hydrochloric acid upon the original color, which is thereby considerably changed. Goode and Perkin also note the action of ammonia upon the original color, but do not find the action of service in preparing standards.

From the evident effect of even a slight amount of moisture we were

<sup>14</sup> Ibid., 31, 596 (1898).

<sup>15</sup> Loc. cit.

<sup>16</sup> Archiv. d. Pharm., 237, 121 (1899).

<sup>17</sup> Loc. cit.



led to adopt the suggestion of Panzer,<sup>18</sup> as applied to the standard Marsh mirrors, for the preservation of our standards. A clean, dry, glass tube, about 5 mm. in diameter, is sealed at one end, at which is placed a small quantity of phosphorus pentoxide covered by a bit of dry cotton wool. The strip is then inserted, colored end down, fastened by a drop of Canada balsam, and the tube is sealed. The set of standards prepared in this way can be used for several months, although the brilliancy of the color is lost after a few weeks.

The color band may be developed by treatment with rather concentrated hydrochloric acid, of a normality of about 6 (one part acid to one of water). This is done in a small test tube, at a temperature not exceeding 60° and for not over two minutes, else, with this concentration of acid, the paper is likely to become disintegrated. The strip is then thoroughly washed with running water and dried. The color on the wet strip is a brilliant dark red in the higher values, while the smaller amounts show a deeper yellow than in the initial set. The length of the bands is considerably greater than that of the original. On drying, the color becomes duller. These bands must also be sealed as above with phosphorus pentoxide, and are somewhat more permanent than the initial set. Figure 2 (Plate 1) represents the set obtained by development of the initial set with hydrochloric acid.

If the original color band is treated for a few minutes with normal ammoniac hydroxide, a dense coal black color is produced, of slightly greater length than the original. This color is far more permanent than the others, but it is nevertheless necessary to seal the dry strips in glass, using fresh, powdered quicklime instead of phosphorus pentoxide. Figure 3 (Plate 2) shows the set obtained by development of the initial set with ammonia.

#### GENERAL PRECAUTIONS.

As far as concerns the reduction of the arsenic, no other precautions are necessary than those which must be observed in the proper conduct of the Berzelius-Marsh method when applied to small amounts. The solution to be reduced should contain no interfering organic matter, nor any metals which prevent or retard the formation of arsine. Sulphur in any form reducible to hydrogen sulphide should be absent. It is well known that small amounts of hydrogen sulphide interfere with the Gutzeit reactions, and it is the custom of most analysts to pass the arsenical hydrogen over paper or cotton wool containing plumbous acetate, or even through a lead solution, before it reaches the mercuric

<sup>18</sup> Zentralbl., 74 (1), 821 (1903).

chloride. As we have been careful to eliminate the sulphur before testing, we have not found this necessary, except in certain cases, when, with a sufficiently long deposition tube, it is very simple to insert a strip of paper saturated with normal plumbous acetate and dried. Phosphites and hypophosphites will also have been oxidized before introduction of the solution, and there is little danger in ordinary work from small amounts of phosphine which might result from the accidental presence of reducible compounds of phosphorus. Antimony should of course be absent, but very small amounts of stibine do not interfere with the recognition, though they may prevent the estimation of arsenic. Free nitric acid must be avoided. Arseniates require especial treatment, as will be discussed below.

#### SPECIAL PRECAUTIONS.

In order to be certain of uniformity in length and color of the bands from the same amount of solution, the following points must be observed:

1. The reduction bottles must be of equal capacity and the deposition tubes of equal bore.
2. The amount of zinc must be the same always, and the granulation must be uniform.
3. The volume and concentration of the acid must be definite.
4. The absorbent cotton must be perfectly clean and reasonably dry, and is therefore best stored in a desiccator before use. The amount used should be approximately the same in all cases, packed in the bulb tube to about the same density.
5. The sensitized paper must be acted upon by a gas in which the moisture is as nearly constant as possible. For this reason the paper cannot be allowed to become moist, nor can the gas be dried. In the first case the band is short and imperfectly shaded; in the second, it is scattered along the whole length of the strip, or even partially escapes the paper. This we have shown by attaching a hard glass tube with capillary, in which, on heating, a mirror of arsenic was obtained. Conversely, under carefully regulated conditions, no evidence of escaping arsenic was found, either by the use of a hot tube or by the introduction of a second strip of sensitized paper.
6. After ten or twelve runs with the same bottle, the atmosphere of the deposition tube becomes too moist, and the bands are consequently too short. It is then necessary to replace the cotton. In order to get a sufficient degree of saturation in the next run, the evolution of hydrogen must go on for a longer time than usual before adding the



test solution, say for an hour. This preliminary saturation may be also conveniently secured by leaving zinc and acid in the apparatus over night.

By observation of the above precautions we have obtained fairly regular and uniform bands of color from equal amounts of arsenic, —

TABLE I.

No. of Analysis.	As <sub>2</sub> O <sub>3</sub> taken.	Total Weight Diluted Solution.	Weight Diluted Solution taken for Analysis.	Reading of Band.	As <sub>2</sub> O <sub>3</sub> found.	As <sub>2</sub> O <sub>3</sub> found, Mean.	Per cent As <sub>2</sub> O <sub>3</sub> found.
	mg.	grm.	grm.	mg.	mg.	mg.	
6	0.05	21.21	5.75 6.05	0.009 0.012	0.033 0.043	0.038	76
8	0.10	24.13	5.74 7.16	0.024 0.027	0.100 0.091	0.096	96
2	0.25	24.95	3.5 2.7	0.037 0.025	0.26 0.23	0.25	100
1	0.50	26.11	1.0 1.3	0.018 0.025	0.47 0.50	0.49	98
7	1.00	25.02	0.39 0.76	0.014 0.028	0.90 0.92	0.91	91
9	1.00	23.76	0.35 0.48	0.013 0.022	0.88 1.09	0.99	99
3	1.50	23.88	0.47 0.47	0.027 0.027	1.37 1.37	1.37	92
4	2.00	25.51	0.66 0.51	0.055 0.035	2.15 1.75	1.95	98
5	2.50	27.04	0.19 0.34	0.015 0.028	2.13 2.24	2.19	88
Average percentage . . . . .							93

using apparatus of definite size, reagents of definite concentration, carefully sensitized paper, and by passing the arsenical gas over the paper in a condition of moisture which is as carefully regulated as possible. Without these precautions, which involve no great care, the method will not give satisfactory quantitative results.

## ANALYTICAL DATA.

The method, as far as it concerns the determination of arsenic in a solution properly prepared for reduction, was tested by the analyses of solutions containing varying amounts of arsenic, which, with the exception of Nos. 5, 8, 7, and 9, were unknown to the analyst (see Table I). In analysis No. 9 the arsenic was present as arsenic acid. In Nos. 5, 8, 7, and 9, the comparison was made with standards which had been kept over three months, and the reading of the bands was confirmed by the standards obtained by development of the initial bands with ammonia.

We do not claim for the method, under ordinary circumstances, a greater accuracy than from five to ten per cent.

## ANALYTICAL NOTES.

*Sensitized Paper.* We have found that the prepared paper, if kept dry and away from the light, does not lose its sensitiveness to a great extent after several months. On long keeping there is apparently a very slight reduction to mercurous chloride, since an old paper after treatment with hydrochloric acid and washing gives a slight darkening with ammonia or auric chloride (for this test, see below). Although this change does not greatly influence the result, it is better not to use paper which has been kept too long.

Contrary to Goode and Perkin,<sup>19</sup> we have found no advantage in using mercuric bromide instead of the chloride. Neither the aqueous solution of the former, which is, in addition, too dilute, nor the alcoholic solution, gives a paper of greater sensitiveness than that prepared from the chloride. The alcoholic solution of the chloride, since it evaporates more rapidly, leaves a less even surface of the salt upon the paper than is obtained by the slower evaporation of the aqueous solution.

*Apparatus.* In case it is necessary to examine larger quantities of solution for arsenic, a larger reduction bottle will naturally suggest itself. In this case, slight variations from the procedure may be found necessary, and the absolute delicacy of the method may be somewhat less.

We have found no sign of arsenical contamination from the rubber stoppers used in the apparatus, and we have therefore not lessened the simplicity of the apparatus by making it entirely of glass. The stoppers are boiled with dilute alkali and washed before use.

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<sup>19</sup> Loc. cit.

Although we have not tried it for ourselves, it would seem obvious that the electrolytic reduction of the solution could be employed if desired.

*Reagents.* From the delicacy of the method, as discussed below, the zinc used by us is evidently highly sensitive. Indeed, the amount of iron present, to which metal, from the work of Chapman and Law,<sup>20</sup> Parsons and Stewart,<sup>21</sup> and others, may be attributed the insensitiveness of most samples of zinc, is about one-seventh of the amount in a zinc which Chapman and Law show to be sufficiently sensitive in the Marsh process.

We have also in this connection studied the effect of the presence of other metals on the sensitiveness of the zinc. The retention of arsenic by the addition of platinic chloride or cupric sulphate, confirmed by one of us<sup>22</sup> (S) several years ago, is well known. With a bright platinum foil in contact with our zinc and using either sulphuric or hydrochloric acid, we have never noticed any loss of arsenic in the Marsh procedure. Similarly, there is no diminution in the delicacy of our method when platinum foil is used. The use of zinc carefully covered with copper after the procedure of Lockemann<sup>23</sup> makes no difference whatever in the results, nor does the addition of tin or lead salts to the solution during the reduction.

The zinc is granulated by pouring the metal, melted in a porcelain casserole, from a height of six feet through a hot porcelain sieve into two feet of cold water.

The estimation of the arsenic in the hydrochloric acid was made on samples of 100 c.c. in two ways. The acid was distilled to half its volume, a treatment which we have shown in the following paper<sup>24</sup> to be sufficient to expel all the arsenic. The distillate was collected in 35 c.c. nitric acid and evaporated with a small amount of sulphuric acid. Again, the acid was allowed to drop slowly into hot nitric acid and the mixture was then evaporated. Several residues obtained by both of these procedures from lots of 100 c.c. gave closely agreeing results, both from the reading of the Marsh mirrors and the Gutzeit color bands. The mean of all determinations was 0.002 mg. for 100 c.c., or 0.02 mg. per liter.

<sup>20</sup> Analyst, **31**, 3 (1906).

<sup>21</sup> Jour. Amer. Chem. Soc., **24**, 1005 (1902).

<sup>22</sup> These Proceedings, **26**, 24 (1891); Amer. Chem. Jour., **13**, 431 (1891).

<sup>23</sup> Zeitschr. f. angew. Chem., **18**, 416 (1905).

<sup>24</sup> These Proceedings, **43**, 327 (1907); Jour. Soc. Chem. Ind., Vol. **26** (1907); Zeitschr. f. anorg. Chem., Vol. **56** (1907).

This acid was shipped in carboy, and we have not observed any increase of arsenic in the acid on standing, such as might result from the action upon the glass if the latter contained arsenic. It is better, however, that such acid should be shipped, or at least stored, whether concentrated or dilute, in ceresine bottles.

We have noticed that the nitric acid from the carboy, which gave no test for arsenic, took up traces from the storage bottle on long standing. We have therefore stored the nitric acid in ceresine. A slight but unimportant amount of paraffine is taken up. 50 c.c. lots of this acid, evaporated with a small quantity of sulphuric acid, gave residues which showed no traces of arsenic. It must be borne in mind that a nitric acid residue contains the arsenic as arsenic acid and that the procedure must accordingly be modified as explained below.

The second sample of hydrochloric acid, referred to in the footnote above, was shipped in ceresine, and the diluted acid is also kept in ceresine. Two 100 c.c. lots of this acid were dropped into nitric acid and evaporated with sulphuric acid. The residues were reduced with sulphurous acid free from arsenic and gave color bands equal to 0.3 and 0.5 mmg. arsenious oxide respectively. This is equivalent to 0.004 mg. of arsenious oxide per liter.

*Procedure.* At the end of a run, a slight annular sublimate is often observed on the inside of the deposition tube where the color band is in contact with the glass. With very small amounts of arsenic this sublimate is white, but is ordinarily slightly colored. It is probably due to transference of mercuric chloride, either through volatilization or capillary action, and a slight color reaction may take place on the deposit. The amount is without influence on the result, but the tube should be cleaned with a bit of dry cotton before being used again.

The temperature during reduction should not be allowed to rise very much, as the moisture equilibrium in the deposition tube is disturbed from the excess of moisture carried over. For this reason the procedure of Bird,<sup>25</sup> which consists in heating the liquid under reduction to the boiling point, is not adapted to this method.

We have found no advantage in using very large amounts of zinc, as recommended by many, especially in the Marsh process, nor do we think it necessary that the zinc should be entirely dissolved.

*Standard Bands.* We have long noticed that solutions of the dilution of 0.01 mg. per cubic centimeter undergo a change on standing,

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<sup>25</sup> Loc. cit.

with the result that a given volume will not yield the same depth of band as when first prepared, or, in the Marsh process, the same intensity of mirror. In more dilute solutions the change is very rapid, and solution IV, containing 0.1 mmg. per cubic centimeter, is of no value as a standard in a day or two. The use of boiled water for dilution greatly retards the change, which would lead to the conjecture that the reaction might be one of oxidation, with formation of arsenic acid, which, as shown below, does not give the same depth of color in a given time as its equivalent of arsenious acid. Yet the treatment of an old solution with sulphurous acid does not increase the amount of arsenic from a given portion of it, as far as we have been able to determine. Solution IV (0.1 mmg.) should be freshly prepared before use; solution II (10 mmg.) will hold its strength for a few weeks, and solution I (1 mg.) should not be used if it has stood for a very long time.

The deposit of color is of course on both sides of the paper. If the strip exactly bisects the tube and the flow of hydrogen is the same in both segments, the intensity of color should be the same on each side of the strip. It often happens that there is a slight difference, and in consequence the band may appear on one side greater than the standard, on the other less. The set of standards is also a series of mean, though not greatly varying color densities, and when viewed from one side or the other may not seem regularly graded. The set should be mounted in such a way that both sides of the strip can be examined, and the mean density of the test band should be compared with the mean density of the standard. The judgment is greatly assisted by treating the band or its duplicate with hydrochloric acid or ammoniac hydroxide (particularly the latter), and comparing the result with the corresponding standards.

*Treatment of the Bands.* Whatever may be the formula of the red compound, it is probable that the reaction is only complete in the presence of an excess of hydrochloric acid. As previously mentioned, the color fades completely on treatment with hot water. Cold water brings about a gradual fading, but this is succeeded by a secondary reaction by which a gray substance is formed. This action of water was further studied by treatment with sodic acetate. A set of standard bands was immersed in half-normal sodic acetate for two hours in the cold. The red color gave place to a uniformly graded light yellow with a tinge of orange. The set, after pressing between filter paper, was then sealed while still moist. In twenty-four hours the yellow had changed to a dull white, with no color except in the higher values.

On the next day there was a change to a faint gray, becoming darker on further standing.

The black color with ammoniac hydroxide suggests the presence of mercurous chloride, but it is not clear whether a decomposition into mercurous chloride takes place before the black color is formed. If the red band is treated with hydrochloric acid, washed, and then placed in ammoniac hydroxide, the color is not an intense black, but rather grayish in tone.

Another reaction of interest is that with auric chloride. If the band, after treatment with hydrochloric acid, is placed in a small test tube with a few drops of hundredth normal auric chloride and allowed to stand for five or ten minutes, a beautiful purple color results. The reaction is characteristic for larger amounts of arsenic.

The reaction of the formation, development, and decomposition of the color bands are susceptible of various interpretations, but, as we have said before, a quantitative study is necessary before expressing an opinion, not only as to the formula of the red body and the mechanism of its formation and decomposition, but also on the existence of intermediate yellow compounds or their formulae.

Bird<sup>26</sup> has applied Bettendorff's reaction to the stains, substantially as follows: The disk of paper containing the color is extracted with one or two cubic centimeters of warm, concentrated hydrochloric acid. The extract is oxidized by a few drops of bromine in hydrochloric acid and treated in a small test tube with an equal volume of 30 per cent stannous chloride. On warming, the pinkish brown color appears.

#### INTERFERENCE OF THE HYDRIDES OF SULPHUR, PHOSPHORUS, AND ANTIMONY.

There is considerable confusion in the statements of various authors as to the color stains from these gases on mercuric chloride paper, and even Bird's more careful study is open to the common criticism that the descriptions are not given with reference to known amounts of the hydrides. In determining to what extent these substances interfere in our method, we have at first ascertained by trial how much of the particular hydride will give a comparable band on the mercuric chloride paper under the same conditions, — particularly in the same time. We then studied the effect of a given treatment upon each color band, and afterward compared the effect of each reagent upon the four approximately equivalent bands.

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<sup>26</sup> Loc. cit.



*Hydrogen Sulphide.* In a freshly prepared solution of sulphurous acid, which gave no test for arsenic, the amount of sulphur was determined by titration with iodine. A solution was made containing 1 mg. of sulphur per cubic centimeter, and from this, in turn, a second containing 0.01 mg. Of this solution amounts corresponding to 10, 30, 50, and 70 mmg. sulphur were added to separate reduction bottles and the action continued for thirty minutes. Bands of a pale yellow were obtained, slightly darker in shade than those from phosphine. The respective lengths corresponded to those from 2, 25, 30, and 40 mmg. arsenious oxide. Fresh strips of paper were now substituted and each experiment was continued for thirty minutes longer. No additional band was obtained from the first; from the others the values were approximately 1, 5, and 10 mmg. This shows that under the same conditions and in equal time the band from 50 mmg. sulphur will be of about the same length as that from 30 mmg. of arsenious oxide, and further, that the reduction of the sulphurous acid is not completed in thirty minutes, like the arsenic, but requires a longer time.

The color of the sulphur band is somewhat brightened by hydrochloric acid (6 N) but not essentially changed, nor was the length increased. Auric chloride produced a dirty light brown. Ammonia on the original band gave also a light brown color.

*Phosphine.* A sample of sodic hypophosphite, containing no arsenic on testing, was shown by analysis to contain 28.94 per cent of oxidizable phosphorus (theory, 29.23). Of this a solution was made containing 1 mg. of phosphorus per cubic centimeter, from which two others were prepared having 0.1 and 0.01 mg. to the cubic centimeter. Of the last solution, 10, 30, 50, and 70 mmg. were reduced for thirty minutes in separate bottles. From 10 mmg. no color was obtained, from 30 mmg. a very faint indication, and from 50 and 70 mmg. bands corresponding in length to only about 2 and 10 mmg. of arsenious oxide respectively. After continuing the action for thirty minutes longer, with fresh strips, there was again no color on the first, a faint indication on the second, and about 1 and 10 mmg. on the third and fourth. It was evident that the reduction was very slow. Next were taken 100, 300, and 500 mmg. After thirty minutes the length of the first band corresponded to about 2 mmg. of arsenious oxide, the second 30, and the third 50, showing that not over one tenth of the phosphorus had been reduced in the given time. On opening the bottles the odor of phosphine was strong.

To obtain a band from the hypophosphite equal to that from 30 mmg. arsenious oxide in the standard time, an amount equivalent

to 200 or 300 mmg. phosphorus is necessary. The color of the bands was a bright yellow, somewhat resembling that from hydrogen sulphide. Hydrochloric acid makes the band a bright lemon yellow, but without increasing its length. The yellow turns slowly brown when exposed to light. Auric chloride acts very slowly, giving at first a characteristic brownish red, which changes to purple. Ammonia acts more slowly than on the arsenic band, giving a less intense black.

*Stibine.* The solutions used were made from a sample of pure tartar emetic, which had been shown to be free from arsenic. They contained respectively 1.0, 0.1, and 0.01 mg. of antimonious oxide per cubic centimeter. Volumes corresponding to 10, 30, 50, and 70 mmg. of the oxide were added to separate bottles and the reduction carried on for thirty minutes. No color was obtained in any case. Hydrochloric acid did not develop. Auric chloride brought out slowly a purple color, duller finally than that of a similarly treated arsenic band. Ammonia turned the band quite quickly black, and a comparison with the arsenic ammonia standards showed amounts equal to about 20 to 40 per cent of the arsenic values. On further reduction for thirty minutes, with fresh strips, there was no additional deposit on the paper which could be developed by ammonia. Continuing the experiments, it was found necessary to add 100 mmg. of antimonious oxide before any visible band was obtained, and 200 mmg. before the band appeared to be of the same length as that from 30 mmg. of arsenious oxide. The color was a faint gray when first visible; darker with increasing amounts. The development with hydrochloric acid and auric chloride or with ammonia showed of course that the paper had been originally affected over a much greater length than was then visible.

These results agree with those obtained by Franceschi,<sup>27</sup> who found by the action of stibine on mercuric chloride a white body to which he gave the formula  $\text{SbHHg}_2\text{Cl}_2$ , analogous to the formula assigned by him to the red arsenic compound. Doward,<sup>28</sup> also, was unable to obtain a stain on mercuric chloride paper from 0.01 to 0.1 mg. of tartar emetic, while from 0.2 mg. he got a faint blackish brown color, a result which is essentially confirmed by our experiments.

*Comparative Effect of Reagents.* From the necessary amounts of each substance, as shown by the above trials, approximately equal color bands were prepared from arsine, stibine, phosphine, and hydro-

<sup>27</sup> L'Orosi, **13**, 397 (1890).

<sup>28</sup> Jour. Chem. Soc., **79**, 715 (1901).



gen sulphide, with a reduction of thirty minutes' duration. Each set of four was then treated with various reagents and the effects compared.

**Initial Band.** The arsenic band appears in a few minutes and is nearly complete before the others begin to form. The deposit is characteristic and unmistakable. The phosphorus and sulphur bands are a uniform pale yellow, rather difficult to distinguish from each other. The antimony band is a faint gray.

**Exposure to Air.** On standing over night in rather moist, warm air, the arsenic band was slightly bleached, the others unchanged. On longer exposure the phosphorus band was turned slightly brown on the upper side, and the sulphur band became slightly dark on the upper edge. Heating to  $105^{\circ}$  had no additional effect on any of the bands.

**Cold Water.** The initial set was placed in cold water. After fifteen minutes the antimony band was bleached completely, the phosphorus became paler, while the arsenic and sulphur were unchanged. After fourteen hours the arsenic was considerably bleached, but was still orange red, while the phosphorus had become a very faint yellow and the sulphur was unchanged.

**Hot Water.** The set was boiled with water for one minute. The arsenic and antimony bands were changed to a grayish white, the phosphorus was bleached to a faint yellow, while the sulphur was unchanged. On standing, the sulphur band became light brown.

**Hydrochloric Acid.** The set was warmed to  $60^{\circ}$  with hydrochloric acid (6 N) for one minute and thoroughly washed. The arsenic band was lengthened and became the usual brilliant red. The antimony was turned slightly gray. The phosphorus became a brilliant lemon yellow, and the sulphur was also brightened, but not so strikingly. On drying, the colors became duller, and on the upper end of the sulphur band was a fringe of dark gray.

**Auric Chloride.** The dried set from the last treatment was immersed in auric chloride (n/100) for five minutes. The arsenic band became at once a brilliant purple; the antimony changed more slowly. The phosphorus slowly turned a characteristic red brown, then to purple, and the final colors of these three bands differed chiefly in intensity. The sulphur band had only a slight brownish tinge.

**Ammonia.** The set was placed in normal ammoniac hydroxide for five minutes. The arsenic band became at once a brilliant black; the antimony also quickly, but the band was longer and duller in shade. The phosphorus turned slowly black and was not equal finally to the other two in intensity. The sulphur band was not blackened, but changed slightly to a pale brown, somewhat darker on drying.

From these results it will be seen that if we have a color band from pure material, within or above the range of the 4 mm. arsenic standards, the differentiation of arsenic from antimony, phosphorus, and sulphur is perfectly simple. With smaller amounts, or especially with mere traces, there can be no confusion with antimony, since stibine gives no yellow color on the paper. With sulphur, while the small initial band might be mistaken for arsenic, the treatment with hot water, ammonia, and auric chloride will easily identify it. But with phosphorus there is likely to be a doubt if the 2 mm. band<sup>29</sup> is very small, since the amount and length of the color do not permit the same comparison as in the larger bands. As we have shown, however, that even as much as 0.1 mg. of phosphorus gives very little color in thirty minutes of reduction, and as this is a quantity which can be easily oxidized in the preparation of the solution for analysis, we should have little to fear from smaller amounts than 0.1 mg. Such amounts might be considered quite accidental.

*Effect of Hydrogen Sulphide, Phosphine, or Stibine on the Arsenic Band.* Very different is it, however, when the arsenic solution also gives by reduction as much of any one of these gases as would alone yield a band equal to the arsenic band in length. This is shown by the following experiments.

**Hydrogen Sulphide.** Amounts of the respective solutions, equal to 30 mmg. of arsenious oxide and 50 mmg. of sulphur, were added together to a bottle and reduced for thirty minutes. Instead of the short, well-defined band of the arsenic, a band nearly three quarters of the length of the strip was formed, of a reddish yellow color. Hydrochloric acid turned it slightly redder, but the appearance was not definitely characteristic of arsenic. On another similar band ammonia brought out splotches of black on a red ground. The arsenic had evidently acted as an accelerator in the reduction of the sulphurous acid, and the resulting band was due to a mixture of the arsenic and sulphur compounds, spread over a greater surface.

**Phosphine.** Solutions containing 30 mmg. arsenious oxide and 200 mmg. phosphorus were added to a bottle and reduced for thirty minutes. The band was longer than the corresponding band of arsenic, but with the characteristic appearance of the latter,—well shaded, except that it was somewhat lighter at the top. Hydrochloric acid converted the color to the well-marked red of arsenic and the length agreed with the hydrochloric acid standard for 30 mmg. Auric

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<sup>29</sup> For the use of the 2 mm. band, see below.

chloride acted more slowly than with arsenic alone, giving a slight brownish red at first and finally a somewhat lighter purple than the pure arsenic color. There was apparently little increase in evolution of phosphine in the presence of the arsenic, and the arsenic compound in the mixed band was not appreciably obscured.

**Stibine.** Solutions containing 30 mmg. arsenious oxide and 70 mmg. antimonious oxide were reduced together for thirty minutes. The resulting band was pale red in color and over twice as long as the band from 30 mmg. of arsenious oxide. Hydrochloric acid gave a color not essentially different, which faded on drying to a rather dirty brownish red. The evolution of the two hydrides was apparently more rapid than either alone, and the mixed band was longer than from either amount.

It is evident from the above results that if we have with the arsenic an amount of hydrogen sulphide even below that required to give a band of the same length as the arsenic, the latter will be so altered as to make its quantitative estimation impossible and its detection doubtful. But, as unavoidable amounts of hydrogen sulphide would be held back completely by lead acetate paper, we should have no difficulty in estimating the arsenic if the solution had not been properly oxidized before testing. Even if the solution contains considerable reducible sulphur, the lead acetate paper will protect the mercuric chloride strip.

We have also little to fear from phosphine, since we should not put a solution into the reduction bottle until the phosphorus had been oxidized as completely as possible. Accidental amounts of phosphine would not affect the quantitative estimation of the arsenic. We have not thought it necessary, for this reason, to verify the statement of Doward<sup>30</sup> that phosphine is held back by cuprous chloride in hydrochloric acid solution, nor have we sought any other reagent which could be adapted to this purpose under the conditions of our method.

In the presence of stibine arsenic may be qualitatively recognized, but not quantitatively determined, when the amount of antimony is enough to give, if alone, an ammonia band equal to that of the arsenic. But we should not test a solution without getting rid of any antimony it might contain, and the methods for that purpose are satisfactory. Slight traces of antimony would not affect the determination.

If the arsenic is accompanied by any two or all three of the substances in question, cases which we think would seldom arise, their in-

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<sup>30</sup> Loc. cit.

fluence on the determination of the arsenic could be predicated from the foregoing investigation.

To sum up, then, we think that small amounts of arsenic can be determined by our method without danger of interference from sulphur, phosphorus, and antimony, provided the solution to be tested is freed as carefully as possible from these substances and the additional precaution is taken to place a strip of lead acetate paper in front of the test paper.

From the comparative rarity of the hydrides of selenium and tellurium and the unlikelihood of their occurrence in ordinary practice, we have made no study of their action on mercuric chloride paper. One would suppose from analogy, also, that the reactions in small amount would be similar to that of hydrogen sulphide. We note in this connection that Rosenheim<sup>31</sup> states that hydrogen selenide has no influence on the Gutzeit test, unless in large quantity, if lead acetate paper is used.

The results of the above experiments are tabulated for comparison as follows :

TABLE II.

REACTIONS OF COLOR BANDS WITHIN THE RANGE OF THE ARSENIC STANDARDS FROM APPROXIMATELY EQUIVALENT AMOUNTS OF ARSINE, STIBINE, PHOSPHINE, AND HYDROGEN SULPHIDE.

Element.	Amounts taken for Reduction.	Initial Band.	Action of Air.	Cold Water.	Hot Water.	Hydrochloric Acid.	Auric Chloride.	Ammonia.
As	30 mmg. (As <sub>2</sub> O <sub>3</sub> ).	Orange yellow to red	Slightly faded	Considerably bleached	Grayish white	Dark red	Bright purple	Dense black
Sb	200 mmg. (Sb <sub>2</sub> O <sub>3</sub> ).	Faint gray	Unchanged	Bleached	Grayish white	Grayish	Dull purple	Dull black
P	200 mmg. (P).	Pale yellow	Pale brown where exposed to light	Considerably bleached	Faint yellow.	Bright lemon yellow	Red brown to purple	Gray black
S	50 mmg. (S).	Dull yellow	Unchanged	Unchanged	Unchanged. On standing, light brown.	Brighter yellow	Slightly brown	Pale brown.

<sup>31</sup> Chem. News, 83, 277 (1901).

## THE PROCEDURE IN PRESENCE OF ARSENIATES.

It is well known that the reduction of an arseniate solution to arsine goes on more slowly than that of an arsenite. This is provided for in the Marsh procedure by continuing the reduction for a longer time when arsenic acid is present; fully an hour, or, if small amounts are present, still longer. The deposition of the mirror being in a comparatively small compass, its size and appearance are not appreciably changed, within the range of the standards, by the slower accumulation of the arsenic particles. In the Gutzeit procedure the case is different for two reasons. The formation of the color bands is over a greater surface and the standard set is based on the deposition of the color in a short time, which, in turn, depends upon a comparatively quick reduction of the arsenious acid. Not only will some arsenic escape reduction during this time, if arsenic acid is present, but the slower congregation of the particles will result in a shorter band. Hence, from a given amount of arsenic as arseniate, the reading of the color after thirty minutes is invariably low. The subsequent reduction may be studied fractionally for sixty to ninety minutes, with successive strips, although the colors from the last fractions may only be shown by the 2 mm. strips (see below). The proportion of color within thirty minutes has been shown by us from repeated trials to be reasonably definite. It is rarely over 50 per cent of the standards, rarely under 40 per cent, and the bands formed are somewhat denser in appearance. This implies that the band from an arseniate, though shorter, contains more arsenical substance than a band of the same length from an equivalent amount of arsenite, and this is borne out by the fact that the subsequent color estimations from the continued reduction do not apparently carry the total percentage of arsenic to more than 80.

There are two ways of approximately estimating the value of the color bands derived from arseniates. We may either make a series of standards from known amounts of arsenic as arsenic acid, with which the test band from an arseniate may be compared, or we may multiply the reading of the ordinary standards by 2 or 2.5. Either of these alternatives will answer, more simply the latter, — though both are obviously inexact, — if one's object is only to get a rough idea of the amount of arsenic present. The estimation can be made, however, within the ordinary limits of the method, if the arseniate is converted to arsenite before reduction to arsine.

Before arriving at the procedure finally adopted, we studied the effect on the reduction of an increase of temperature and also that of various catalyzers. A solution containing 10 mmg. of arsenious oxide

as arsenic acid was prepared by evaporating 10 c.c. of solution I repeatedly with nitric acid and making up to one liter. The bottles were heated during the reduction in an air bath in such a way that all above the necks protruded. At 60° the bands obtained from 3 c.c. of the arseniate solution after thirty minutes of reduction were only about 43 per cent of the standard for 30 mmg. of arsenious oxide. Parallel trials with 3 c.c. of the arsenite solution gave bands of the standard length. Another experiment at 90° gave no better results. The bands from the arseniate solution were not over 50 per cent of the standard, while the parallel arsenite reductions gave shorter bands than at ordinary temperature, owing to the larger amount of moisture carried over. That a reduction at the boiling point would cause a practically complete conversion to arsine, as claimed by Bird, seems improbable, while the moisture equilibrium would be so disturbed as to invalidate the procedure.

Returning to the reduction at ordinary temperature, it was found that no increased effect was produced within the standard time by the addition of stannous chloride or potassic iodide. Platinum in contact with the zinc, even when the acid was more concentrated, was of no service, and the use of copper-covered zinc did not help. An appreciable increase but not a complete reduction was effected by sesquisulphate of titanium. It was evident that the use of a catalytic agent did not solve the problem with such small amounts of arsenic, and we were therefore forced to a reduction of the arseniate to arsenite before testing. For this purpose we found sulphurous acid the simplest substance, since comparatively little is needed, no excess of reagent need be left in solution, and it can easily be prepared free from arsenic.

The sulphurous acid solution was made from pure copper and pure sulphuric acid, and was saturated at 0°. The solution gave no test for arsenic when tested in quantities larger than would be used in an analysis. The tests were made after boiling out the sulphur dioxide from the samples.

We tested the efficacy of the sulphurous acid as follows: Four portions of the arsenic acid solution, corresponding to 10, 20, 30, and 40 mmg. of arsenious oxide, were evaporated in small glass dishes with 6 c.c. of the sulphurous acid until the excess of sulphur dioxide was apparently expelled. On adding the residues to the reduction bottles, the color bands came up quickly as in the case of arsenites, and in thirty minutes all the bands were equal to the corresponding standards in length and intensity of color. Subsequent trials conducted similarly confirmed these results. The precaution was taken to use the lead



acetate paper, on which in some cases there was a slight deposit of the sulphide.<sup>32</sup>

In practice, when the solution contains an arseniate, or when the substance has been oxidized, say by nitric acid, one may add a sufficient quantity of sulphurous acid to the entire solution or to the aliquot portion taken for reduction. In analysis No. 9, Table I, we followed the latter plan, adding 10 c.c. of sulphurous acid in two parts, the second after partial evaporation. The excess of sulphur dioxide is then expelled, but the evaporation must not be carried too far, as chlorides, if present, would cause a loss of arsenic. In testing the residues the lead acetate paper should be used.

#### THE ABSOLUTE DELICACY OF THE METHOD.

For most practical purposes the set of standards from 2 to 70 mmg. is sufficient. Amounts of arsenic between 2.0 and 0.5 mmg. can be approximated by the 4 mm. strip, but in studying the limit of delicacy we have allowed the action to take place within a smaller compass. The ordinary strip is cut in two, and these pieces are again divided lengthwise, giving a piece 2 mm. wide and 35 mm. long. This is inserted in a tube of slightly more than 2 mm. in diameter, which is fitted into the usual deposition tube by a washer of rubber tubing. With these small strips a series of standards may be made from 10 mmg. down. The yellow color appears definitely, though of course slightly, from 0.5 mmg. Treated with hydrochloric acid, ammonia, or hydrochloric acid and auric chloride, the indication is much sharper, and from this amount up to 10 mmg. the gradation of the 2 mm. standards is well marked. From 0.3 mmg. the yellow color is exceedingly faint, but development with the reagents brings it out. At 0.2 mmg. the formation of yellow is no longer seen, but treatment with hydrochloric acid gives a faint but definite color, which under the glass is seen to be greater than the effect produced by 0.1 mmg. Development with ammonia or auric chloride is also definite. From 0.08 mmg. a faint fringe of color is visible under the glass after treatment with hydrochloric acid, and the indication is even sharper with ammonia or auric chloride. From 0.05 mmg. no results were obtained. These tests were made on two solutions, prepared at different times.

Between 0.05 and 0.08 mmg. is clearly the limit at which we have been able to detect any arsenic by the mercuric chloride paper under the conditions of our method. It is safe to set this limit at 0.08 mmg.

<sup>32</sup> We have found that the lead acetate paper is more sensitive to hydrogen sulphide than the mercuric chloride.

(0.00008 mg.) of arsenious oxide, which is equivalent to 0.00006 mg. of metallic arsenic or one seventeen-thousandth of a milligram.

In the above tests, on quantities under 10 mmg., the hydrochloric acid containing 0.004 mg. arsenious oxide per liter was used. This, in 15 c.c. of the diluted acid, assured a quantity of arsenic far below the above limit, while blank tests of over an hour's duration gave negative results. The deposits from these small amounts were formed within thirty minutes, and each reduction was continued thirty minutes longer.

Although the method is a very delicate one, as shown by the above tests, we are far from claiming that 0.08 mmg. of arsenious oxide can be recognized by it with certainty under the varying conditions of analytical practice. We are not so much concerned with the absolute delicacy, however, as with the amount which may be considered a practical limit, the recognition of which is definite under all conditions, and which, when obtained from an aliquot portion of a solution, may safely be used as a factor in the quantitative determination of the arsenic. In this particular we agree fully with Chapman and Law,<sup>33</sup> who have expressed the opinion that in the Marsh method 5 mmg. should be taken as a practical limit, and that one's efforts should be directed toward recognizing this amount with certainty. We consider, therefore, that 1 mmg. (0.001 mg.) of arsenious oxide may be set as the practical limit of our method, although less than one tenth of this amount may be recognized under favorable conditions. The color produced on the large or small strip by 1 mmg. need not be confused with that from hydrogen sulphide, stibine, or phosphine, if these are unavoidably present, while the more minute traces of color, though not easily confounded with those from the first two, are similar in appearance to that from the last. We have found by trial that 0.1 mmg. of arsenious oxide, if present as arseniate, can be recognized after reduction with sulphurous acid.

Previous estimates of the delicacy of the Gutzeit test have not been under 0.1 mmg., so far as we know, with the exception of that made by Dowzard,<sup>34</sup> who states that one fifteen-thousandth to one twenty-thousandth of a milligram can be recognized by the modification described by him. This figure is practically the same as ours.

#### THE USE OF THE METHOD.

The method naturally suggests comparison with the Marsh in the present accepted form of the latter. In the modification described by

<sup>33</sup> Zeits. f. angew. Chem., 20, 67 (1907).

<sup>34</sup> Loc. prim. cit.



one of us (S.) in 1891,<sup>35</sup> in which a standard set of mirrors was employed for the first time, the absolute limit of delicacy was placed at 1 mmg. of arsenious oxide. The most important improvement in procedure which has been made of late years is the cooling of the capillary tube, described by Gautier,<sup>36</sup> Thomson,<sup>37</sup> Lockemann,<sup>38</sup> and others. By this means the scattering of the deposit of arsenic is prevented and the mirror takes a more compact and hence more easily identifiable form. In spite of this advantage, we have not been able, as yet, to reach the absolute limit of delicacy in the Marsh process which is set by Thomson at 0.4 mmg. of arsenious oxide, by Lockemann and others at 0.1 mmg. arsenic. We cannot think that this failure is due to insensitiveness of the zinc, but to other reasons not yet discovered. Sanger and Gibson<sup>39</sup> have shown, for example, that the nature of the antimony mirror depends upon the kind of glass tubing used, and they suggest that a greater or less oxidation of the stibine may take place in the accidental presence of air, if the glass contains a catalyzing agent. If this were true, it is easy to imagine a slight retention of the arsenic from the same cause, since the oxide formed would be fixed by the base of the glass. This point will be soon investigated in this laboratory.

Not only, as far as our experience goes, has the Gutzeit method proved to be more sensitive than the Marsh, but we think it will be found so by others. In certain lines of work, in which the sample may be tested directly or quickly freed from interfering substances, the Gutzeit in the form proposed by us may be preferable to the Marsh, particularly when the routine analysis of a large number of samples is concerned. In toxicological or legal work it will serve as a valuable adjunct to the Marsh method, since the exhibits from both methods can be presented and will corroborate each other, qualitatively or quantitatively. Though not convertible, like the Marsh mirror, to a definite and obvious compound of arsenic, yet the color band can be easily differentiated from the effect produced by other substances on mercuric chloride.

We have not studied the application of the method to the analysis of many products, though we have used it successfully for the determination of arsenic in wall paper, in the urine, and in certain salts.

<sup>35</sup> Loc. cit.

<sup>36</sup> Bull. Soc. Chim., **27**, 1030 (1902).

<sup>37</sup> Chem. News, **88**, 228 (1903); also, **94**, 156 and 166 (1906).

<sup>38</sup> Loc. cit.

<sup>39</sup> These Proceedings, **42**, 719 (1907); Jour. Soc. Chem. Ind., **26**, 585 (1907); Zeits. f. anorg. Chem., **55**, 205 (1907).

Its usefulness will depend upon its adaptability to the needs of the analyst, and it may be modified to meet his conditions. For instance, in the examination of beer, if the analyst *must* add the sample to the reduction bottle without previous treatment, there should be adequate provision for the retention of hydrogen sulphide, the prevention of frothing, etc. We are not at all sanguine of the success of the method, however, unless the test solution has had adequate treatment before reduction.

During the study of the interference of sulphur, phosphorus, and antimony, as given above, the possibility of quantitatively determining small amounts of these substances by this method, particularly of antimony, suggested itself. We desire to note also that the principle of allowing the gas to be tested to act along the surface of the reacting substance has a useful application in other cases, notably in the determination of fluorine, and we are at present engaged in developing a method for the estimation of small amounts of that substance according to this principle.

In conclusion, it gives us pleasure to acknowledge our indebtedness to the C. M. Warren Fund of Harvard University for material assistance in the preparation of the colored plates used in this article.

HARVARD UNIVERSITY, CAMBRIDGE, MASS., U. S. A.,  
August, 1907.

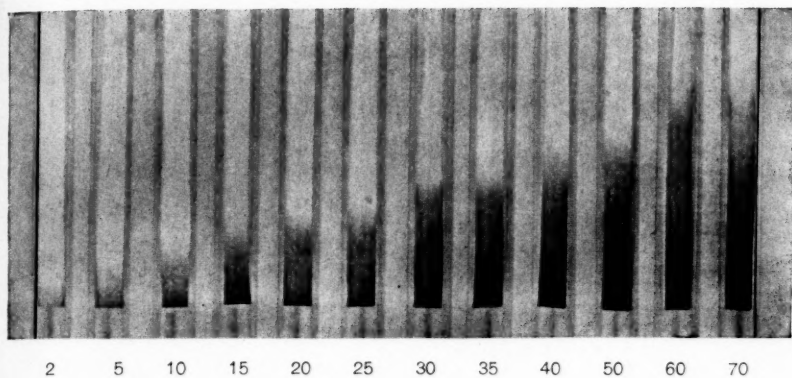


FIG. 1.

STANDARD ARSENIC BANDS IN MICROMILLIGRAMS OF  $\text{As}_2\text{O}_3$   
INITIAL.

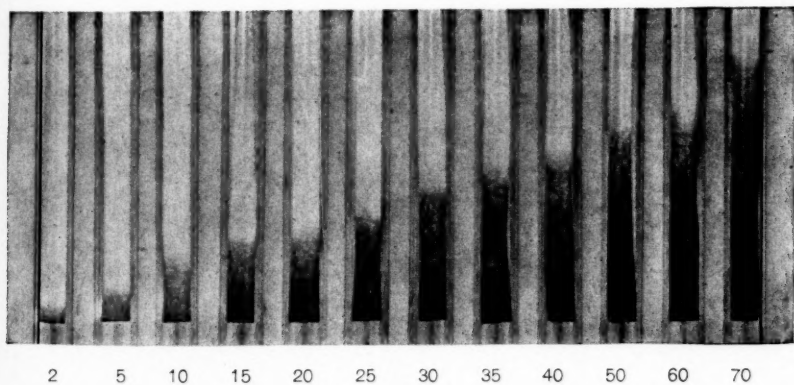
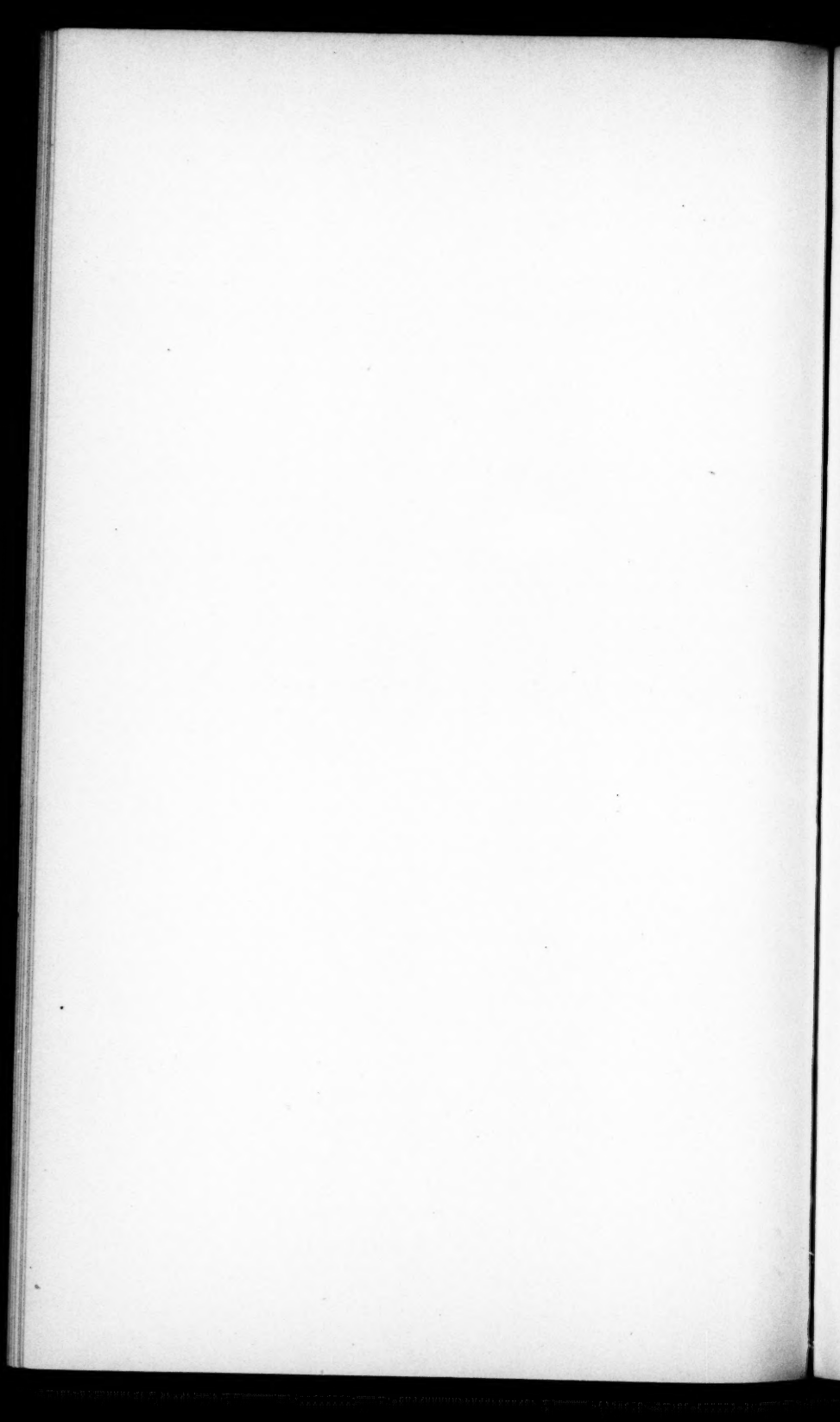


FIG. 2.

STANDARD ARSENIC BANDS IN MICROMILLIGRAMS OF  $\text{As}_2\text{O}_3$   
HYDROCHLORIC ACID DEVELOPMENT.



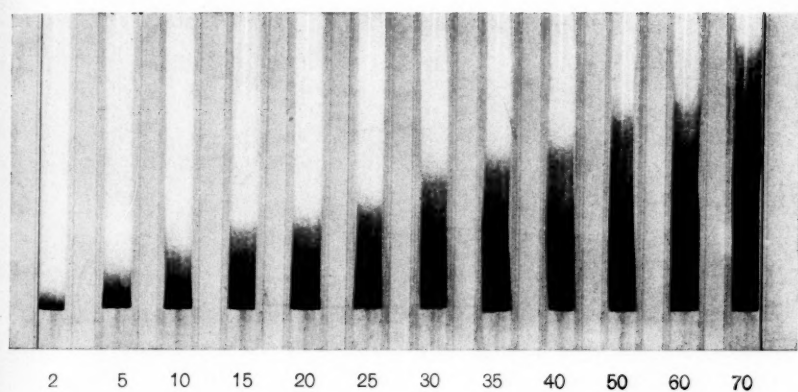


FIG. 3.

STANDARD ARSENIC BANDS IN MICROMILLIGRAMS OF  $\text{As}_2\text{O}_3$   
AMMONIA DEVELOPMENT.



